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PROCESS AND DEVICE FOR MANUFACTURING ULTRAFINE INORGANIC POWDERS BY AEROSOL-LASER COUPLING

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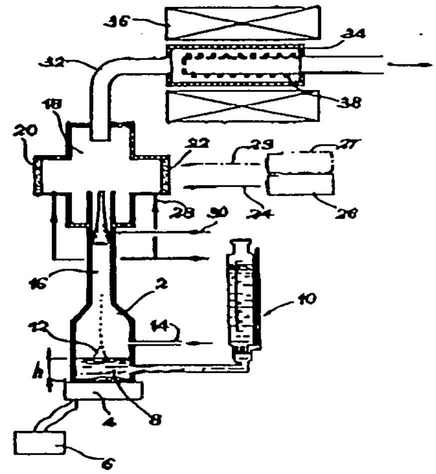
The process for manufacturing an ultrafine powder from an inorganic material comprises the following stages: a) preparation of a solution (8) containing at least one solvent capable of absorbing a laser beam and at least one precursor of the powder; b) ultrasound spraying (12) of the solution to form droplets of this solution; c) entrainment of the droplets by at least one entrainment gas (14); d) at least one laser irradiation (24,29) of a droplet-entrainment gas combination at a determined wavelength to form particles of said material, this wavelength being

absorbable by the droplet solvent; and e) drying (36) of the particles, the stages b to e of the process being carried out under a controlled atmosphere.



Description

The object of this invention is a process for manufacturing inorganic ultrafine powders by coupling of aerosols and laser irradiation as well as a device for implementing this procedure. The powders may be powders of one or more metal oxides or nonoxides, as well as powders of metal alloys.

The ultrafine powders obtained are intended for use particularly in the manufacture of ceramics or vitroceramics as well as superconducting materials that can be used in numerous applications, particularly to make surface coatings, and for chemical, thermal, or mechanical protection of certain materials (antiabrasive or anticorrosive protection).

These powders can also be used to make transparent coatings used particularly in optical guides, or they may be used to make reflective or antireflective layers.

These powders may also be used to manufacture materials with dielectric, pyroelectric, piezoelectric, or ferroelectric properties; these materials are used in the fields of microelectronics or optoelectronics.

All these coatings and materials are obtained essentially by fritting, compacting, and densification of the manufactured powders.

In particular, the process of the invention permits the production of powders from zirconium oxide, aluminum oxide, silicon dioxide, silicon nitride and/or carbide, titanium oxide or boride, zinc or yttrium oxide, YBaCuO, and alloys of carbon, tungsten, and cobalt.

At present, one method for obtaining ultrafine powders is pyrolysis of aerosols produced by ultrasound spraying. This process is known as the pyrosol process.

The following are examples of documents illustrating the production of powders by the pyrosol process:

- the article by N. Mizutani and T. Liu, "Synthesis of Spherical Si_3N_4 Powders by Spray Pyrolysis of Polysilazane," in: Ceramic Transactions, vol. 12, Ceramic Powder Science III, eds. G. L. Messing et al., 1990, pp. 59-73;

- the article by P. Odier et al., "Processing of Ceramic Powders by the Spray Pyrolysis Method; Influence of the Precursors. Examples of Zirconia and $YBa_2Cu_3O_7$." Id. pp. 75-89;

- the article by T. Liu et al., "Preparation of Spherical Fine ZnO Particles by the Spray Pyrolysis Method Using Ultrasonic Atomization Techniques," J. Mat. Sci. 21, 1986, pp. 3698-3702;

- the article by Y.C. Lau et al., "Synthesis of Zirconia Powders in an RF Plasma by Injection of Inorganic Liquid Precursors," in: Ceramic Transactions, vol. 1, Ceramic Powder Science II, A., Ohio, 1988, pp. 298-303.

In the first three documents, the ultrafine powders are obtained by heating the aerosols in a kiln. In the last document, a radiofrequency plasma is used to produce the powders.

The object of the invention is a new process for the manufacture of ultrafine powders based on the pyrosol process, as well as a device for implementation of the process. This process makes it possible to obtain ultrafine powders at a lower cost than the known processes. In addition, these powders present excellent properties making it possible to obtain densified items having improved thermomechanical products as well as higher fritting kinetics than those currently used.

More specifically, the object of the invention is a process for manufacturing an ultrafine powder from an inorganic material, comprising the following stages:

a) preparation of a solution containing at least one solvent that can absorb a laser beam and at least one precursor of the powder;

b) ultrasonic spraying of the solution to form droplets of this solution;

c) entrainment of droplets by at least one entrainment gas;

d) at least one laser irradiation of the droplet-entrainment gas ensemble at a determined wavelength to form particles of said material, this wavelength being absorbable by the droplet solvent, and

e) drying of the particles

stages b to e of the process being carried out under a controlled atmosphere.

This process makes it possible to obtain submicron, even nanometer powders, i.e. powders with particle diameters from 5 to 100 nm, with a high yield. These powders are also monodispersed, equiaxial, relatively nonagglomerated, and of high purity.

The solution to be sprayed may consist of one or more liquid precursors of the powder or of an aqueous or nonaqueous solution containing one or more solvents and one or more precursors dissolved in the solvent or solvents.

In order for the solution to be sprayed ultrasonically, it must generally have a low viscosity—lower than 5 mPa·s. Also, to adapt the viscosity of certain solutions, they must be mixed with one or more solvents of lower viscosity. Other ultrasound spraying techniques make it possible to use liquids with a viscosity of 20 to 50 mPa·s.

The precursor concentration in the solution depends essentially on its viscosity.

Depending on the composition of the solution, laser absorption may occur only at the level of the solvent or solvents, or it may occur at the level of the precursors and the solvents.

According to the invention, it is possible to use a single wavelength to irradiate the droplet-entrainment gas combination, which [radiation] can be absorbed by the precursor, the solvent, the entrainment gas, or one of their combinations. It is also possible to use several different irradiation wavelengths, each wavelength being specific to one or more absorbing products.

For example, it is possible to irradiate the droplet-entrainment gas combination with two different laser wavelengths, the first being absorbable by the solvent and the second being absorbable by the precursor in solution, the entrainment gas, or by both of them.

Thus, by combining the laser absorption by the solvent and the laser absorption by the precursor of the powder and/or the entrainment gas, we achieve a significant increase in the yield of the transformation of the precursor into powder.

According to the invention, laser irradiation may be continuous or pulsed.

According to the invention, the entrainment gas may consist of one or more gases, reactive or nonreactive, that may or may not absorb the laser emission. The term "reactive gas" means a precursor gas of the powder.

For example, the entrainment gas may consist of an inert gas only (nitrogen, rare gases), an inert gas containing a sensitizer such as ammonia, sulfur hexafluoride (SF_6), silicon tetrafluoride (SiF_4); a reactive gas such as air, oxygen, ammonia, or hydrogen used alone or in combination with a sensitizer.

In particular, ammonia may constitute by itself a reactive entrainment gas that is sensitive to the laser radiation used.

The wavelengths used extend from the infrared to the ultraviolet, passing through the visible, and are a function of the sensitive products used as well as the type of powder to be made. In general, infrared radiation is used. This can be accomplished with a CO_2 laser having adjustable or nonadjustable wavelength.

Drying of the particles by irradiation is carried out at a temperature higher than the boiling point of the solvent when it has a boiling point lower than that of the precursor; otherwise it is lower than the boiling point of the precursor. Therefore, this temperature is a function of the solvent and/or the precursor used. In practice, heating ranges from 100°C to 600°C.

The process of the invention is carried out in a reactor with a controlled atmosphere. Thus, it is possible to work in an atmosphere without oxygen and to form nonoxide powders.

The ultrasound frequency used is a function of the desired particle size for the powder. In fact, the size of the vaporized droplets, and therefore of the powder particles, is directly connected to the ultrasound frequency; the diameter of the droplets decreases when the ultrasound frequency increases. Therefore, it is advantageous to work at high frequency. The most viscous solutions can no longer be pulverized.

In practice, we use ultrasound frequencies selected in the range of 10 to 3500 kHz, preferably between 30 and 2500 kHz.

The precursor or precursors of the powder may be soluble monomers or polymers with low molecular weight. They may be mineral, organic, or organometallic, as well as solids or liquids.

These precursors may be used directly in dissolved form or may be made up in situ.

When the resulting powder contains oxygen atoms, the chemical reactions brought into play in situ for manufacture of the precursors are hydrolysis (action of water) and polycondensation. At the same time, when the resulting powder is a compound without oxygen, the reactions brought into play for in situ manufacture of the precursors are ammoniolysis (action with ammonia) followed by polycondensation.

In particular, with the invention it is possible to obtain nanometric powders of nonoxide ceramics such as powders of carbide, nitride, boride, carbonitride, and silicide.

These powders without oxygen are obtained from precursors without oxygen. Examples include the formation of a ceramic based on nitrogen, carbon, and silicon from silazanes or polysilazanes.

These silazanes or polysilazanes may be used as is, dissolved in a solvent without oxygen, or formed in situ. For these purposes, direct ammoniolysis is used between a first liquid precursor in an organic solvent and the ammonia used as the entrainment gas for the droplets of solution.

As the first precursor in the solution that can be used in the invention to make polysilazanes, examples include dichlorosilane, trichlorosilane, and methyldichlorosilane or ethyldichlorosilane.

The process of the invention also makes it possible to obtain oxide powders. These oxide powders are obtained by using one or more solid mineral or organic salts dissolved in an aqueous

solution or in a solvent, preferably an oxygenated one. They may also be obtained from metallic alkoxides dissolved in an oxygenated solvent.

The oxygenated solvent may be a solvent with one or more oxygen atoms in its molecule, or a solvent without oxygen atoms in its molecule. In the latter case, the oxygen may come from the air, or it may be pure oxygen, which then forms the entrainment gas.

The mineral salts used may be nitrates, chlorides, acetates, or carboxylates.

The solvents used depend on the precursor used and the nature of the desired powder (oxide or nonoxide). In addition, these solvents must have low viscosity to permit spraying of the solution, for example, lower than 5 mPa·s. In addition, these solvents may or may not be capable of absorbing the laser wavelength. Sensitizers can also be added to them.

Examples of solvents that can be used in the invention and that do not contain an oxygen atom in their molecules are aromatic compounds such as benzene, toluene, xylene, or acetonitrile, the primary and secondary amines, and also ethylenediamine.

In particular, polysilazanes are soluble in these solvents.

Examples of solvents that can be used in the invention and that have oxygen atoms in their molecules are alcohols, ketones, short-chain ether oxides generally having 1 to 5 carbon atoms, such as ethanol, propanol, butanol, acetone, acetylacetone, or ethyl ether.

Sensitizers that are added to a solvent and that do not absorb radiation are alcohols, ketones, ether oxides and the aromatics cited above.

Another object of the invention is a device for embodiment of the process of the invention. This device includes:

- a spray vessel to hold the solution to be sprayed, closed on its base by a piezoelectric transducer;
- a means for maintaining the level of the solution in the spray vessel constant, this level being equal to the ultrasound focal distance of the transducer;
- an ultrasound generator connected to the piezoelectric transducer;
- an irradiation cell with transparent windows at the selected irradiation wavelength, mounted downstream from the spray vessel;
- at least one laser that can generate at least one laser beam of the desired wavelength;
- a first transport nozzle to connect the spray vessel to the irradiation chamber;
- a powder recovery device housed in a kiln;
- a second transport nozzle to connect the irradiation cell to the recovery device;
- at least one entrainment gas delivery pipe mounted above the irradiation cell.

The spray vessel, the irradiation cell, the transport nozzles and the powder recovery device form a unit of which the atmosphere can be controlled.

Other characteristics and advantages of the invention will become more apparent from the description to follow, given as a nonlimiting illustration, with reference to the single attached figure which is an outline of an apparatus for implementation of the invention.

The device represented on the single figure for implementation of the process according to the invention includes a spray container or vessel 2 with symmetrical revolution, having on its lower part a piezoelectric transducer 4 (lead ceramic-zirconium, PZT) connected to an ultrasound generator 6. The disk-shaped pellet 4 forms the bottom of the spray vessel 2. The generator 6 delivers ultrasound typically of 150 W and a frequency of 800 kHz.

The level h separating the surface of solution 8 to be sprayed, contained in container 2, and the surface of the piezoelectric pellet 4 should be equal to the focal distance of the piezoelectric pellet. The focalization of the ultrasound waves at the surface of the solution permits expulsion of the droplets 12.

To assure a constant level h, a graduated reservoir 10 with a constant level is connected to the base of the container 2. This makes it possible to control in situ the quantity of liquid 8 consumed as the spraying proceeds.

An entrainment gas, which may or may not be reactive, is introduced into the middle part of the container 2 by means of a pipe 14.

A transport nozzle 16 brings in the aerosols formed to the base of an irradiation cell 18 with symmetrical revolution, according to the axis of the cell. The irradiation cell 18 is mounted downstream from the spray vessel 2, and its axis is merged with that of the spray vessel 2.

This cell 18 is cross-shaped in its configuration. It has lateral windows 20 and 22 which are transparent to the laser beam 24, and which constitute, respectively, an entry window and an exit window for the laser beam. These windows 20 and 22 are parallel to each other and to the flow of aerosols, and perpendicular to the laser beam 24.

These windows 22 and 20 are made of a transparent material between 9 and 11 μm, when a CO_2 laser 26 is used, such as alkaline halides (NaCl, KCl, etc.) or zinc selenide (ZnSe).

This CO_2 laser 26 may be a power laser emitting at 10.6 μm or an adjustable laser in a wavelength between 9 and 11 μm, designed to carry out infrared irradiation with successively two or more wavelengths.

In some cases, it is possible to use a second CO_2 laser 27, which may or may not be adjustable, emitting a beam 29 parallel to the beam 24.

On the lower part of the irradiation cell 18 there are also gas feeds 28 and 30, respectively, for delivery of inert gas (nitrogen, argon) intended, respectively, for sweeping of the windows 20 and 22 and entrainment of the powder produced in the irradiation cell 18; the sweeper gas feed is peripheral, whereas the entrainment gas feed is axial.

The gas introduced in 28 allows for cooling of the windows 20 and 22, as well as cleaning from these windows of the particles produced in the irradiation cell.

A transport nozzle 32 situated in the extension of the nozzle 16, and at the exit of the irradiation cell 18, makes it possible to deliver the particles produced in the irradiation cell to a powder collector 34 placed inside a kiln 36 designed for drying of the particles. The powder collector is a filter permitting only passage of the entrainment gases that have not reacted, as well as the gases produced in situ.

The resulting powder is referenced as 38.

The kiln 36 delivers a temperature higher than the boiling point of solution 8, typically between 100°C and 600°C.

The flow of the entrainment gases and that of the sweeper gas are typically chosen at from 2 to 10 L/min.

According to the invention, the unit formed by the spray vessel, the irradiation cell, the powder collector, and the nozzles constitutes a sealed, closed reactor in which the atmosphere is controlled.

The device represented on the single figure makes it possible to preserve the advantages of a powder synthesizing laser process from gaseous or very volatile precursors, that is, a zone of photons-laser-reagent interaction, clearly delimited and separated from the cold walls of the reactor, with very fast temperature increases, resulting from the laser interaction, short residence times of the reagents in the laser beam, and high quenching speeds of the particles formed.

This device results in ultrafine powders with particles 5 to 100 nm in diameter. These powders are monodispersed, equiaxial, relatively nonagglomerated, and of high purity.

Below we give examples of the manufacture of ultrafine powders according to the invention.

Example 1: Synthesis of composite powders based on silicon, carbon, and nitrogen

In this example, the precursor to be pyrolyzed is a relatively viscous liquid polysilazane. Thus, to favor the formation of aerosols, the viscosity of this precursor must be lowered by adding a solvent to it, such as a nonoxygenated aromatic compound or acetonitrile. The polysilazane represents from 10% to 60% by volume of the solution to be sprayed.

This polysilazane can be manufactured as described in the article by N. Mizutani, cited above.

The aromatics such as benzene, toluene, and xylene, as well as acetonitrile present infrared absorption bands at about 9.6 μm, whereas polysilazane presents absorption bands at about 10.6 μm. We then use two CO_2 lasers whose wavelength can be adjusted, and apply a

double infrared irradiation at two different wavelengths, one at 10.6 μm for the precursor, and the other at 9.6 μm for the solvent.

By combining the laser absorption by the polysilazane, powder precursor, and solvent in this way, we obtain an improved yield of powder precursor transformation as compared to the use of a laser irradiation-sensitive precursor alone.

Example 2: Synthesis of ultrafine powders of zinc oxide, ZnO

This synthesis is obtained from aerosols formed by spraying of water-alcohol solutions of zinc nitrate; the resulting zinc oxide powder is used in electronics.

For this purpose, a solution of zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$ is made in a water-alcohol mixture, primary or secondary alcohol, preferably primary. The alcohol acts as a sensitizer in solution.

Coupling with the laser occurs at the level of the C-O vibration of the alcohol.

The entrainment gas is a gas which is not sensitive to laser irradiation, such as air, nitrogen, oxygen, or argon.

Thus, methanol and ethanol can be used as sensitizers; they have an absorption band at 9.5 μm, necessitating the use of a CO_2 laser with adjustable wavelength, and n-butanol which presents an absorption band at 10.6 μm can also be used; this results in the use of an industrial-strength CO_2 laser whose wavelength cannot be adjusted.

The use of alcohol in a zinc nitrate solution also improves the aerosol ultrasound spray yield.

Thus, a 50/50 water-ethanol mixture has an aerosol production yield increased by 70% as compared to the use of water alone.

This spray yield is improved by using alcohols that are highly soluble in water, such as methanol or ethanol, rather than n-butanol, which has a maximum 10% solubility by volume in water.

Example 3: Synthesis of oxide powders

In place of a nitrate solution, a zinc acetate solution in methanol can be used to obtain zinc oxide powders.

Examples 4 and 5: Synthesis of oxide powders

Here the precursors are one or more mineral or solid organic salts, dissolved in a water-alcohol solution as in Example 2. In addition, the entrainment gas contains a sensitizer whose role is, like the alcohol, to absorb the laser emission and to heat the aerosol. One of the

best choices of sensitizers in the entrainment gas is SF_6 (absorption at 10.6 μm) which makes it possible to use industrial-strength CO_2 lasers.

The use of SiF_4 as a sensitizer would probably result in the formation of SiO_2 by reaction with the water in the solvent.

Any pollution due to the elements forming the gaseous sensitizer requires thermal treatment of the powder between 400 and 800°C before it is used (typically annealed in a kiln at 600°C in an inert atmosphere).

Water-alcohol solutions of yttrium nitrate are used to obtain yttrium oxide Y_2O_3 (Example 4) and a water-alcohol solution of yttrium nitrate and zirconyl chloride for the synthesis of the stabilized zirconium (Example 5). For additional details, see the document P. Odier, cited above.

Example 6: Synthesis of composite W-C-Co powders

In this example we use aerosols of an aqueous ammonia solution of H_2WO_4 and $Co(en)_3WO_4$ (with ethylenediamine abbreviated), which is irradiated at 10.6 μm. Laser absorption occurs in the complex $Co(en)_3WO_4$ at the level of the ethylenediamine and in the solvent or the ammonia solution. The latter, under the effect of irradiation, decomposes into $NH_3 + H_2O$; the NH_3 provided can, in turn, absorb the laser irradiation.

The entrainment gas is a neutral gas (argon, nitrogen, etc.) to which SF_6 may be added as a sensitizer.

The conditions of aerosol formation are those described in the article by L. E. McCandlish et al., "Metastable Nanocrystalline Carbides in Chemically Synthesized W-Co-C Ternary Alloys," in: MRS Symp. Proc., vol. 132, ed. Materials Research Society, 1989, pp. 67-72.

Claims

1. Process for manufacture of an ultrafine powder from an inorganic material, comprising the following stages:

a) preparation of a solution (8) containing at least one solvent that can absorb a laser beam and at least one precursor of the powder;

b) ultrasound spraying (12) of the solution to form droplets of the solution;

c) entrainment of the droplets by at least one entrainment gas (14);

d) at least one laser irradiation (24, 29) of the droplet-entrainment gas combination at a specific wavelength to form particles of said material, this wavelength being absorbable by the droplet solvent, and

e) drying (36) of the particles,

stages b to e of the process being carried out in a controlled atmosphere.

2. Process according to Claim 1, characterized in that the solution also contains at least one precursor of the powder that can absorb the selected wavelength.

3. Process according to Claim 1 or 2, characterized in that the entrainment gas is chosen to absorb a laser radiation wavelength.

4. Process according to Claim 2 or 3, characterized in that the droplet-entrainment gas combination is irradiated with two different wavelengths, the first wavelength being absorbable by the solvent, the second wavelength being selected to be absorbed by the precursor and/or the entrainment gas.

5. Process according to any of Claims 1-4, characterized in that the solvent contains a dissolved sensitizer sensitive to the laser wavelength used.

6. Process according to any of Claims 1-5, characterized in that the solvent contains a sensitizer chosen from alcohols, ketones, ether oxides, aromatic compounds without an oxygen atom, and acetonitrile.

7. Process according to any of Claims 1-6, characterized in that the entrainment gas contains a sensitizer sensitive to the laser wavelength used.

8. Process according to any of Claims 1-7, characterized in that the solution contains a first precursor of the powder and the entrainment gas contains a second precursor of the powder different from the first.

9. Process according to any of Claims 1-8, characterized in that the wavelength or wavelengths used are in the infrared.

10. Process according to any of Claims 1-9, characterized in that at least one CO_2 laser (26, 27) is used for the laser irradiation.

11. Process according to any of Claims 1-10, characterized in that the irradiation is applied perpendicular to the flow of the entrainment gas.

12. Process according to any of Claims 1-11, characterized in that the precursor in solution is a liquid organic metal, a mineral salt, or an organic salt, optionally complexed.

13. Process according to Claim 8, characterized in that the first precursor is a liquid organic metal, a mineral salt, or an organic salt, and the second precursor is a gas.

14. Process according to any of Claims 1-13, characterized in that the entrainment gas contains a gas chosen from NH_3, SF_6, and SiF_4.

15. Process according to any of Claims 1-14, for the manufacture of an oxide powder, characterized in that the solution is an alcohol solution of a mineral salt, an organic salt, or a metallic alkoxide.

16. Process according to any of Claims 1-14, for the manufacture of a powder based on silicon, carbon, and nitrogen, characterized in that an organosilane is used as the precursor in solution in a nonoxygenated aromatic compound or in acetonitrile.

17. Device for implementation of the process according to any of Claims 1-16, characterized in that it includes:

- a spraying vessel (2) designed to hold the solution to be sprayed, closed at its base by a piezoelectric transducer (4);
- a means for keeping the level of the solution in the spray vessel constant, this level being equal to the ultrasound focal distance of the transducer;
- an ultrasound generator (6) connected to the piezoelectric transducer;
- an irradiation cell (18) with windows that are transparent to the selected irradiation wavelength, mounted downstream from the spray vessel;
- at least one laser (26, 27) that can generate at least one laser beam (24, 29) of the selected wavelength;
- a first transport nozzle (16) to connect the spray vessel to the irradiation chamber;
- a device (34) for recovery of the powder, housed in a kiln;
- a second transport nozzle (32) to connect the irradiation cell to the recovery device;
- at least one pipe (14, 30) for delivery of the entrainment gas, mounted upstream from the irradiation cell,

the spray vessel, the irradiation cell, the transport nozzles, and the powder recovery device forming a combination whose atmosphere can be controlled.

18. Device according to Claim 17, characterized in that the delivery pipes (28) of a sweeper gas are provided on the periphery of the irradiation cell (18).

19. Device according to Claim 17 or 19, characterized in that a delivery pipe (30) for a powder entrainment gas is provided along the axis of the irradiation cell.

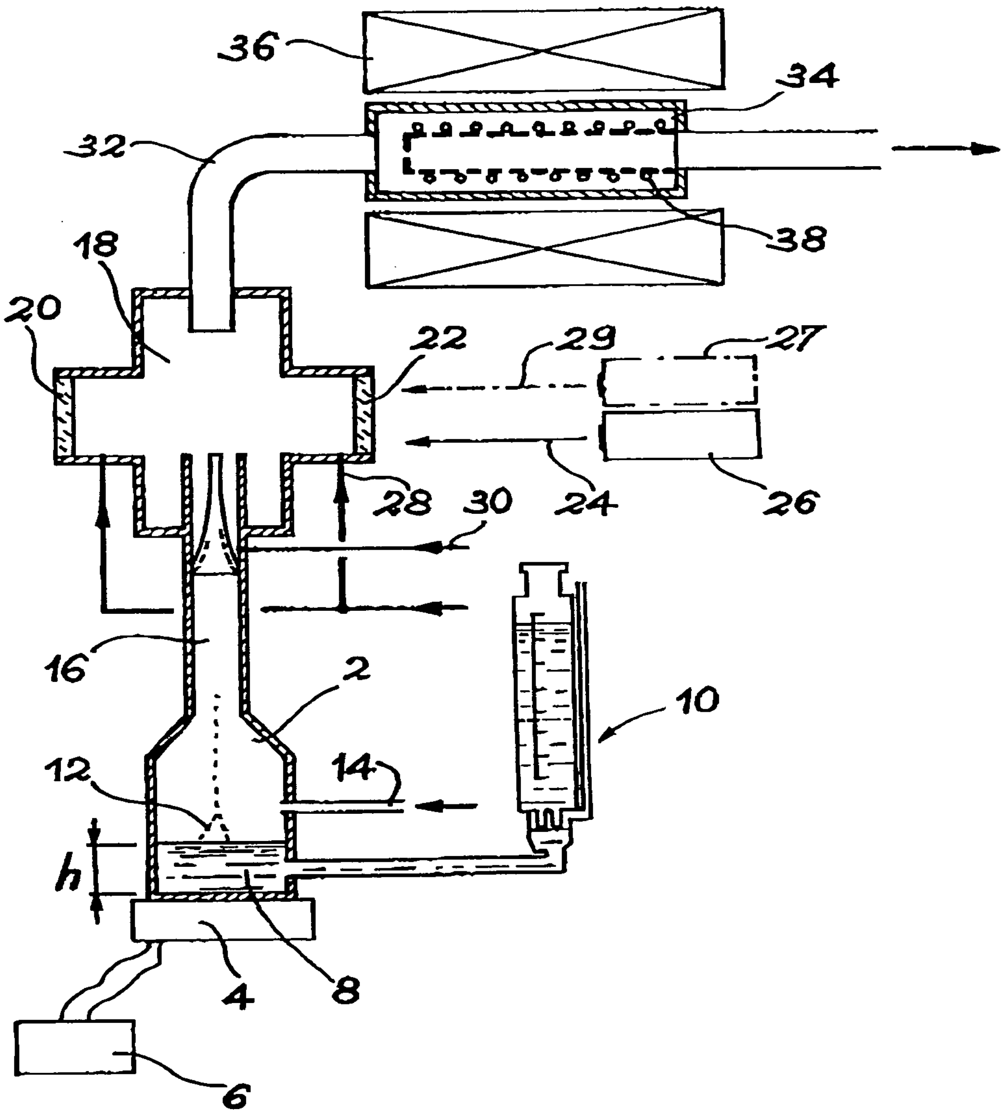


Figure 1